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Preparation and Characterization of New Oxide Ion Conductors in Bi_2O_3-As_2O_5 System

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Abstract : Materials in xBi_2O_3-As_2O_5 binary system: $1 \leq x \leq 7$, were prepared by solid state reaction. XRD shows that single phase materials were formed when x = 5, 5.5, 5.667, 5.75, 6 and 7. The symmetry and space group of the materials were determined. Compositions with $5 \leq x \leq 6.25$ are solid solutions. Electrical properties of the single phase materials were studied using ac impedance spectroscopy at a frequency range of 10 Hz to 13 MHz. These materials are thermally stable and appear to be oxide ion conductors. Highest conductivity was obtained in $Bi_{23}As_4O_{44.5}$ with σ value of 5.66×10^{-5} ohm^{-1} cm^{-1}, E_a = 0.72 eV at 300°C.

Key words: bismuth arsenate, oxide ion conductor

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Introduction

A number of investigations have been undertaken on the crystal structure of materials in the Bi_2O_3-As_2O_5 system; however, studies on the physical properties of these materials are limited. A nonstoichiometric sillenite-type phase was found in the Bi-rich portion of the Bi_2O_3-As_2O_5 system [1]. The authors reported that this phase, with body-centered cubic symmetry, formed solid solutions over an extremely limited range between 6.23 and 6.74 mol % As_2O_5 at 650°C.

The crystal structure of $BiAsO_4$ has been reported [2,3]. In addition, the crystal structure of compositions Bi_2O_3 : As_2O_5 = 4 : 1, 6 : 1 and 7 : 1 were reported [4]. It was postulated that in the structure, square Bi_2O_2 layers were connected via layers of isolated tetrahedral AsO_4 groups. The discovery of Bi_2O_3-As_2O_5 system having structures closely related to that of CaF_2 and δ-Bi_2O_3 [4, 5] initiated research on the electrical properties of these materials since bismuth oxide systems are well known for their high oxide ion conductivity [6].

We have undertaken to study xBi_2O_3-As_2O_5 binary system with x ranging from 1 to 7. Here we report the results on the formation and characterization of these materials.

Experimental

Bismuth arsenate compounds with xBi_2O_3 : As_2O_5; $1 \leq x \leq 7$ were prepared using Bi_2O_3 (99.9%, Aldrich) and As_2O_5 (99.9%, Alfa Aesar) via solid state reaction. Bi_2O_3 was dried at 300°C prior to weighing, while As_2O_5 was dried at 200°C. Stoichiometric mixtures were weighed (*ca*. 4g total), mixed with acetone in an agate mortar, dried and fired in Au foil boats at 900 - 980°C for 48 – 240 h, depending on compositions.

The samples were air-quenched and examined by X-ray diffraction (XRD) using a Shimadzu diffractometer XRD 6000 and $CuK\alpha_1$ radiation (λ = 1.5406 Å). Scans were conducted at scanning range of 10 to 60° 2θ with a scanning rate of 2°/min and a step size of 0.02°. A lower scanning rate of 0.1°/min with step size of 0.01° was applied to collect data for the refinement of selected materials using "CHEKCELL" program. Angle correction was carried out based on Si standard. Elemental compositions of selected samples were determined using inductively-coupled plasma atomic emission spectrometry (ICP-AES, Perkin Elmer P1000).

Pellets for electrical property measurement were cold pressed and sintered at 900°C overnight; Au paste electrodes were then fired on at 200-600°C. The electrical properties were determined by ac impedance spectroscopy using a Hewlett-Packard Impedance Analyzer HP 4192A in the frequency range of 10 Hz to 13 MHz. Measurements were made between 200°C and 850°C by incremental steps of 50°C with 30 min stabilization time. Most

measurements were made in air, and where necessary in oxygen free nitrogen (OFN).

For differential thermal analysis (DTA) and thermogravimetric analysis (TGA), Perkin-Elmer instruments (model DTA 7 and TGA 7) with a heating and cooling rate of $10^oC\ min^{-1}$ were used.

The Scanning Electron Microscopy (SEM) experiments were run on selected materials using SEM JEOL JSM-6400 operated at 15kV, with working distance of 15 mm. Infrared (IR) spectra of selected materials were recorded using a FT-IR Spectrophotometer (Perkin-Elmer Model 1725x).

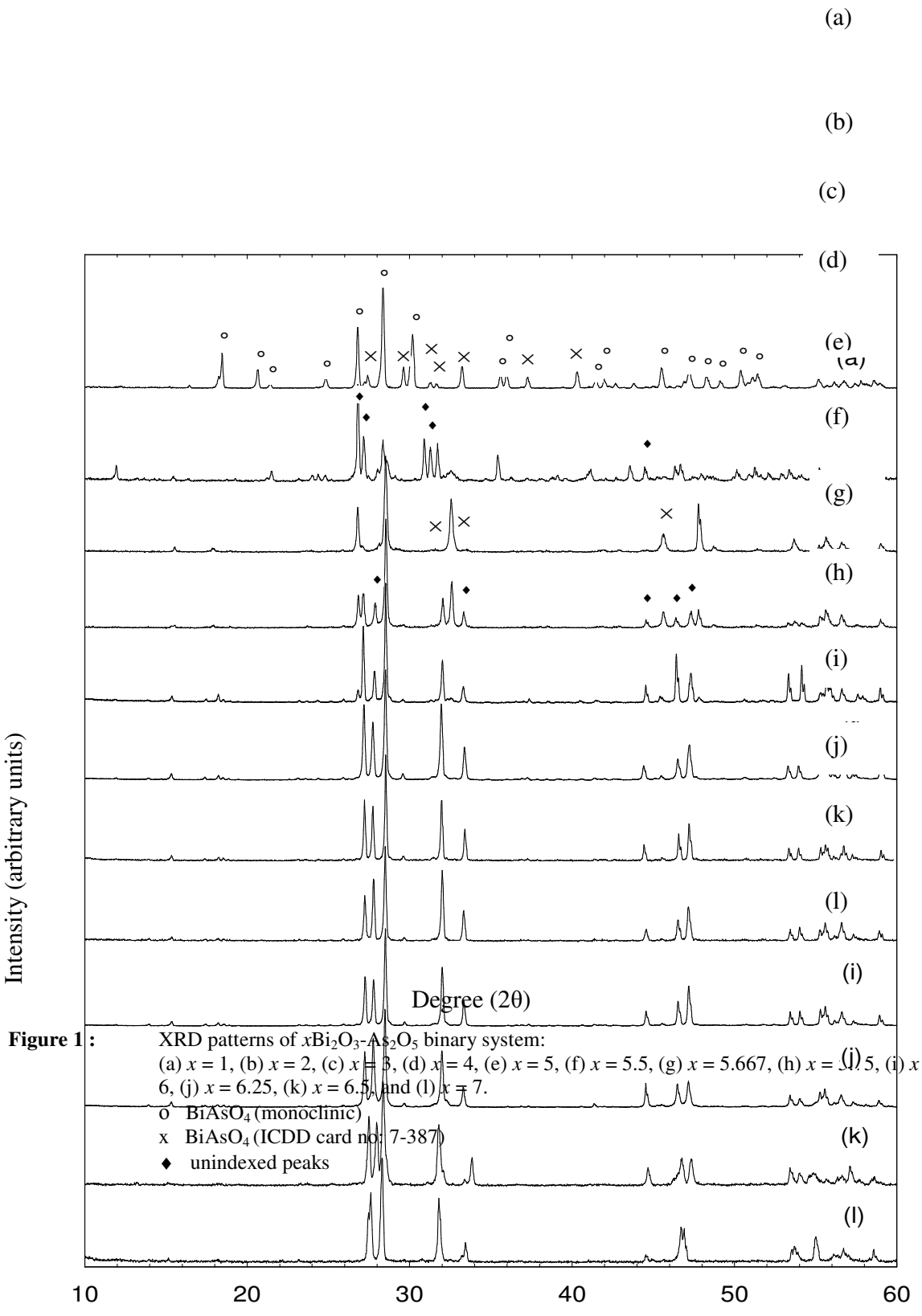

Figure 1 : XRD patterns of xBi_2O_3-As_2O_5 binary system:
(a) x = 1, (b) x = 2, (c) x = 3, (d) x = 4, (e) x = 5, (f) x = 5.5, (g) x = 5.667, (h) x = 5.75, (i) x = 6, (j) x = 6.25, (k) x = 6.5, and (l) x = 7.
o $BiAsO_4$ (monoclinic)
x $BiAsO_4$ (ICDD card no: 7-387)
♦ unindexed peaks

Results and Discussion

Phase purity and stability

Materials with Bi_2O_3:As_2O_5 ratios of 1:1 to 7:1 in Bi_2O_3-As_2O_5 system have been prepared (Fig. 1). Among these materials, $BiAsO_4$, $Bi_4As_2O_{11}$ [4], Bi_3AsO_7 (ICDD card no: 46-191), $Bi_8As_2O_{17}$ [4], $Bi_{12}As_2O_{23}$ (ICDD card no: 44-175), and Bi_7AsO_{13} [4] have been reported as single phase materials. Our XRD results show that under the experimental conditions adopted single phase materials exist only at Bi_2O_3:As_2O_5 ratios of 5:1 and above. At lower Bi:As ratios mixed phase materials were obtained despite prolonged heating or heating at temperatures close to melting. Three different crystal modifications of $BiAsO_4$ have been reported: tetragonal (ICDD card no: 5-573, 47-1850, 85-906), monoclinic (ICDD card no: 25-89, 74-1412) and a phase with unknown crystal symmetry (ICDD card no: 7-387). The XRD pattern of $BiAsO_4$ prepared in this work indicates the coexistence of the monoclinic phase and the phase with unknown crystal symmetry. Refinement of the XRD data of the material of composition $2Bi_2O_3$-As_2O_5 using the lattice constants reported by Jie and Eysel [4] as starting parameters left the major peaks at $2\theta = 26.8^o$, 27.2^o, 30.9^o, 31.3^o and 44.5^o unindexed. The XRD pattern of $3Bi_2O_3$-As_2O_5 was similar to that in ICDD card no: 46-191. However some additional peaks were observed at around $2\theta = 31.7^o$, 33.6^o, and 45.7^o. These peaks could be attributed to the presence of $BiAsO_4$ (ICDD card no: 7-387) as a secondary phase. $4Bi_2O_3$-As_2O_5 was reported to be orthorhombic with cell parameters of a = 5.718 Å, b = 9.985 Å, c = 3.304 Å. [4]. Refinement of the XRD data of $4Bi_2O_3$-As_2O_5 prepared based on lattice values reported left five unindexed peaks at $2\theta = 27.9^o$, 33.4^o, 44.6^o, 46.5^o and 47.3^o, indicating the presence of $Bi_{12}As_2O_{23}$ in the sample.

The compositions of phase pure compounds in xBi_2O_3-As_2O_5 binary system, $5 \leq x \leq 7$ were determined by ICP-AES (Table 1).

Table 1 : Elemental composition of xBi_2O_3-As_2O_5, $5 \leq x \leq 7$

		Atomic %	
x	Element	Calculated	Experimental
5	Bi	31.25	31.52 ± 0.06
	As	6.25	6.06 ± 0.04
	O	62.50	62.42 ± 0.02
5.5	Bi	31.88	32.17 ± 0.04
	As	5.80	5.59 ± 0.03
	O	62.32	62.24 ± 0.01
5.667	Bi	32.08	32.31 ± 0.01
	As	5.66	5.49 ± 0.02
	O	62.26	62.20±0.01
5.75	Bi	32.17	32.51 ± 0.12
	As	5.59	5.35 ± 0.08
	O	62.24	62.14 ± 0.03
6	Bi	32.43	32.63 ± 0.13
	As	5.41	5.26 ± 0.01
	O	62.16	62.10 ± 0.04
6.25	Bi	32.68	32.94 ± 0.02
	As	5.23	5.04 ± 0.01
	O	62.09	62.02 ± 0.01
7	Bi	33.33	33.79 ± 0.10
	As	4.76	4.44 ± 0.07
	O	61.90	61.77 ± 0.03

The atomic percent of oxygen present in the materials was calculated by difference. In general, the experimental values agreed (within errors) with calculated values, thus confirming the compositions of these phases.

Thus, Bi_5AsO_{10}, $Bi_{22}As_4O_{43}$, $Bi_{17}As_3O_{33,}$ and $Bi_{23}As_4O_{44.5}$ appear to be new compounds in Bi_2O_3-As_2O_5 binary system. The XRD pattern of $Bi_{23}As_4O_{44.5}$ is similar to that of $Bi_{23}P_4O_{44.5}$ [10, 13]. This implies that $Bi_{23}As_4O_{44.5}$ and $Bi_{23}P_4O_{44.5}$ could be isostructural. XRD analysis with scan rate of 0.1^o/min, was run on $x Bi_2O_3$-As_2O_5; $5 \leq x \leq 6.25$ over 2θ range of 10 to 60^o. Indexing of their XRD patterns showed that these materials exhibited very similar crystal chemistry (Table 2). These materials were successfully refined in triclinic symmetry with space group of *P-1*. Compositions with Bi_2O_3:As_2O_5 ratios of 5:1 to 6.25:1 appeared to be solid solutions. They have similar XRD patterns with a shift in 2θ at ~ 26.8^o and 46.4^o (Figure 1). It was expected that the increasing Bi content could change atomic arrangement in the structure which would result in a shift in d-spacing. Generally, lattice parameters and volumes of these materials increased with increasing Bi content, thus obeying Vegard's law (Figure 2). The ionic radius of Bi^{3+} (0.96 Å) is larger than that of As^{5+} (0.335 Å) [7]; Bi – O bond length is thus expected to be longer than As – O bond which may lead to an increase in cell parameters of the materials with increase of Bi content.

The material $Bi_{12}As_2O_{23}$ has been reported previously to crystallize in monoclinic symmetry with space group of $P2_1$ (ICDD card no: 44-175; Jie and Eysel [4]). The XRD pattern of $Bi_{12}As_2O_{23}$ is similar to that reported in ICDD card number 44-175. However, peaks at $2\theta = 18.6^o$ and 26.0^o in $Bi_{12}As_2O_{23}$ could not be indexed in the space group $P2_1$ when the refinement was performed based on cell parameters reported in ICDD. On the other hand, peaks at $2\theta = 14.0^o$ and 18.6^o could not be indexed when the refinement was performed based on cell parameters reported by Jie and Eysel [4]. It is, however possible to index all the peaks in $Bi_{12}As_2O_{23}$ in the triclinic symmetry with space group of *P-1* using Chekcell refinement program.

The sample where Bi/As = 6.5 appeared to be a mixture of 6.25:1 and 7:1 phase. The XRD data of Bi_7AsO_{13} were indexed on a monoclinic cell as reported [4].

All the materials studied in $x Bi_2O_3$-As_2O_5 binary system, $5 \leq x \leq 7$ were thermally stable up to 900°C as no weight loss was observed in TGA. No phase transition was observed for these materials in their DTA thermograms.

Table 2 : Lattice parameters of $x Bi_2O_3$-As_2O_5 binary system from X-ray diffraction data

x	Crystal system	Lattice parameters (Å)			Unit-cell volume ($Å^3$)
5	Triclinic	a = 11.4821 (8)	b = 11.5188 (7)	c = 20.5405 (15)	2245.72
5.5	Triclinic	a = 11.4979 (11)	b = 11.5177 (15)	c = 20.5739 (15)	2255.28
5.667	Triclinic	a = 11.5036 (11)	b = 11.5177 (12)	c = 20.5783 (14)	2256.81
5.75	Triclinic	a = 11.5179 (5)	b = 11.5226 (6)	c = 20.6063 (1)	2263.53
6	Triclinic	a = 11.5312 (8)	b = 11.5357 (9)	c = 20.6179 (11)	2271.67
6.25	Triclinic	a = 11.5362 (12)	b = 11.5401 (14)	c = 20.6256 (15)	2274.38
7	Monoclinic	a = 4.0669 (3)	b = 3.8879 (4)	c = 5.3514 (4)	84.61

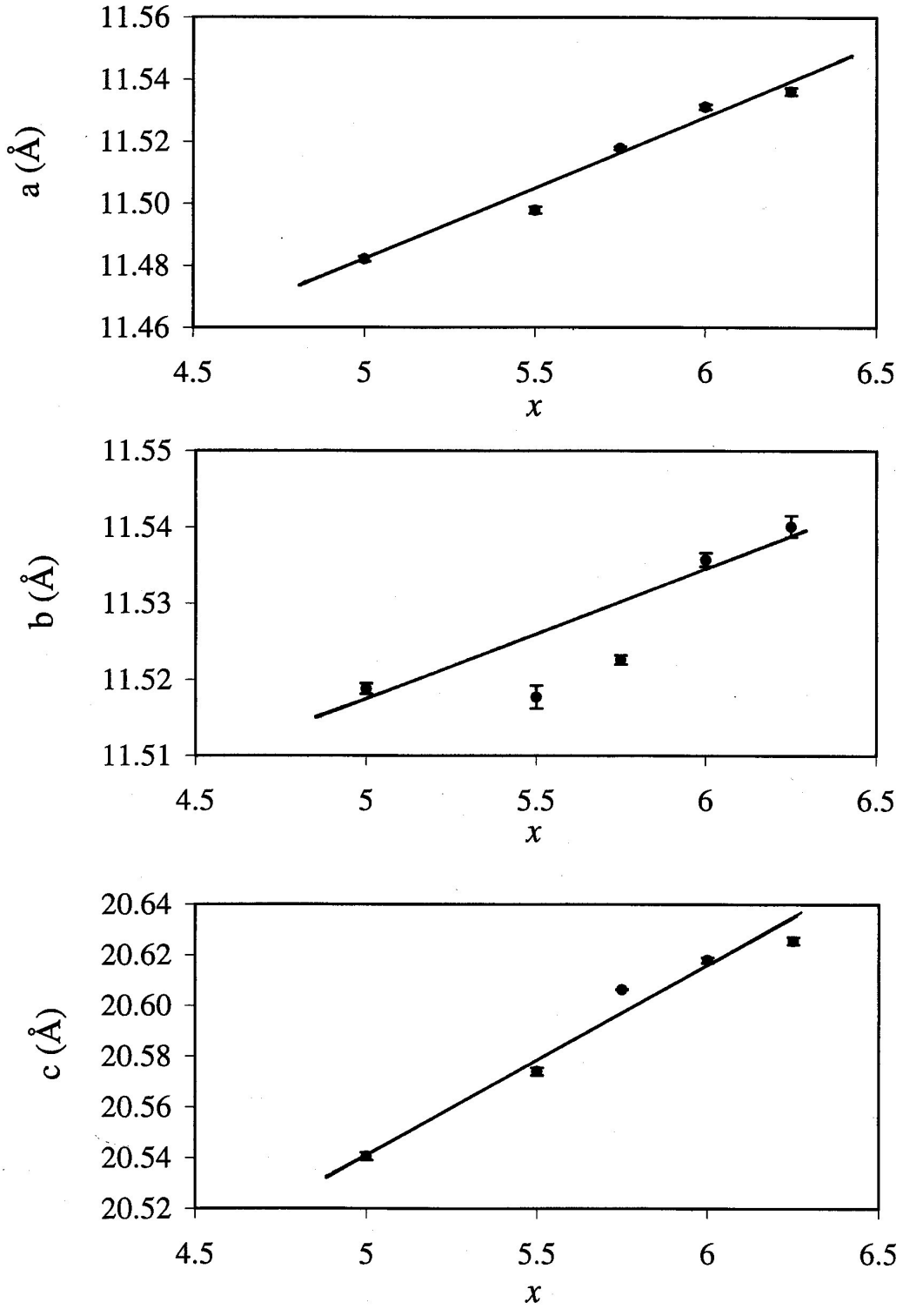

Figure 2 : Variation of cell parameters with Bi content (x) for materials of formula $x Bi_2O_3$-As_2O_5.

Conductivity studies

The conductivity of materials with compositions xBi_2O_3 -As_2O_5, $1 \leq x \leq 7$, has not been reported. Conductivity values were extracted from ac impedance data. In general, a broadened semicircle with a low-frequency spike was obtained for temperatures below 400°C; the spike became more pronounced at higher temperatures. Typical impedance data are shown in Figure 3 for $Bi_{23}As_4O_{44.5}$; at 300°C the associated capacitance of

the semicircle (Figure 3a) has a value of 9.1 x 10^{-12} F cm^{-1}, which is typical of bulk component [8]. At higher temperatures, the predominant feature is a low-frequency spike inclined at ≈ 70° to the horizontal axis (Figure 3b). Its associated capacitance of ≈10^{-6} F cm^{-1} is characteristic of ionic polarization phenomena at the blocking electrodes, and a diffusion-limited Warburg impedance, thus supporting the idea the conduction was predominantly ionic.

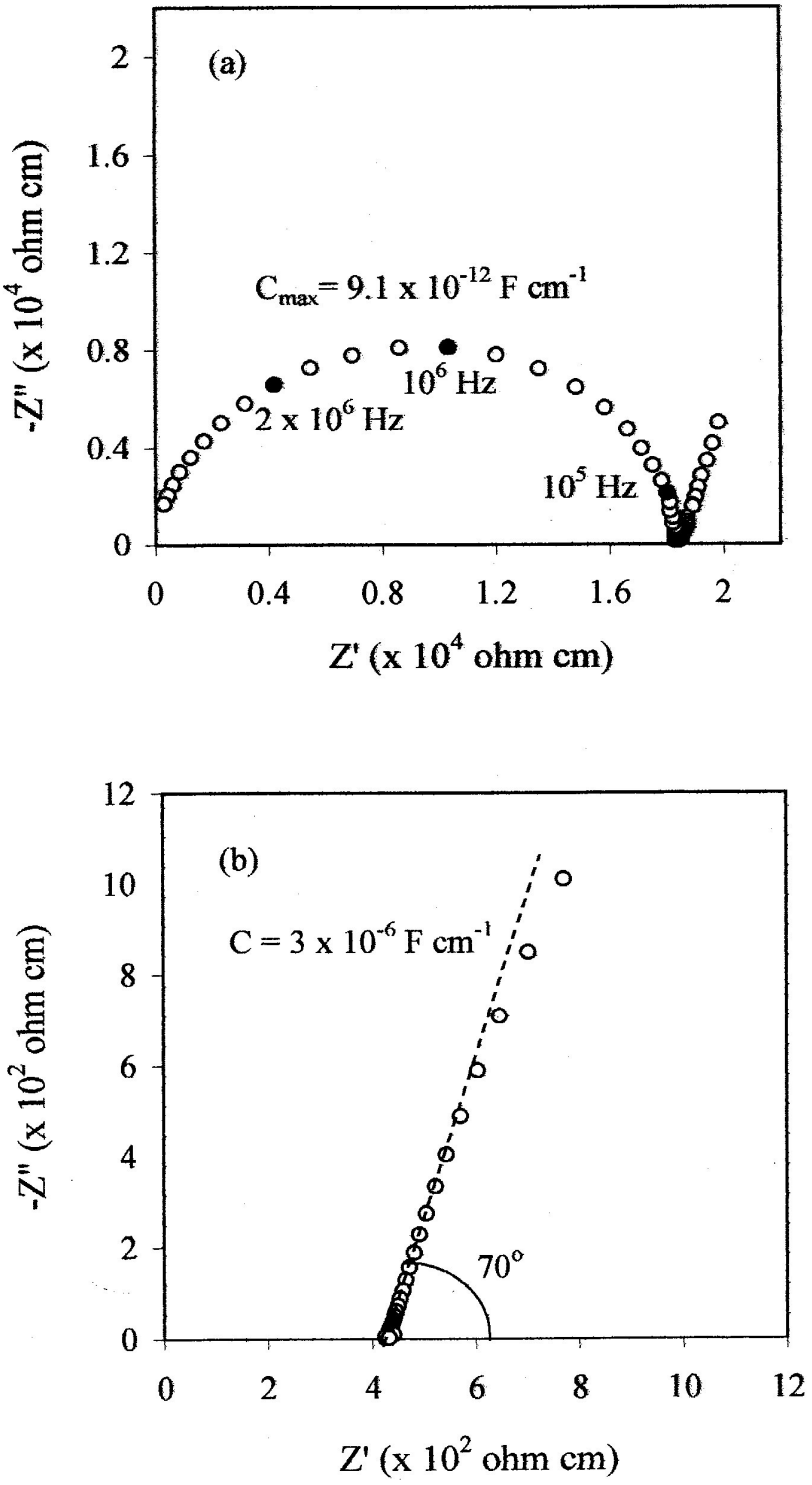

Figure 3 : Impedance data of $Bi_{23}As_4O_{44.5}$ at (a) 300°C; (b) 500°C. Z' and Z'' are the real and imaginary part of the complex impedance Z*, respectively.

In order to confirm the conduction species of the material conductivity measurements were carried out in dry oxygen free nitrogen (OFN). Figure 4 shows such a plot for $Bi_{23}As_4O_{44.5}$. No change in conductivity was seen on changing the atmosphere, indicating that contribution in conductivity by electrons if present is negligible. Similar results were obtained for the other materials studied in xBi_2O_3-As_2O_5 binary system, $5 \leq x \leq 7$. It thus appears that these materials are oxide ion conductors, as have been reported for the phosphate analogues [9, 10]. EMF measurements of an oxygen concentration cell containing these materials as the membrane are needed in order to confirm this.

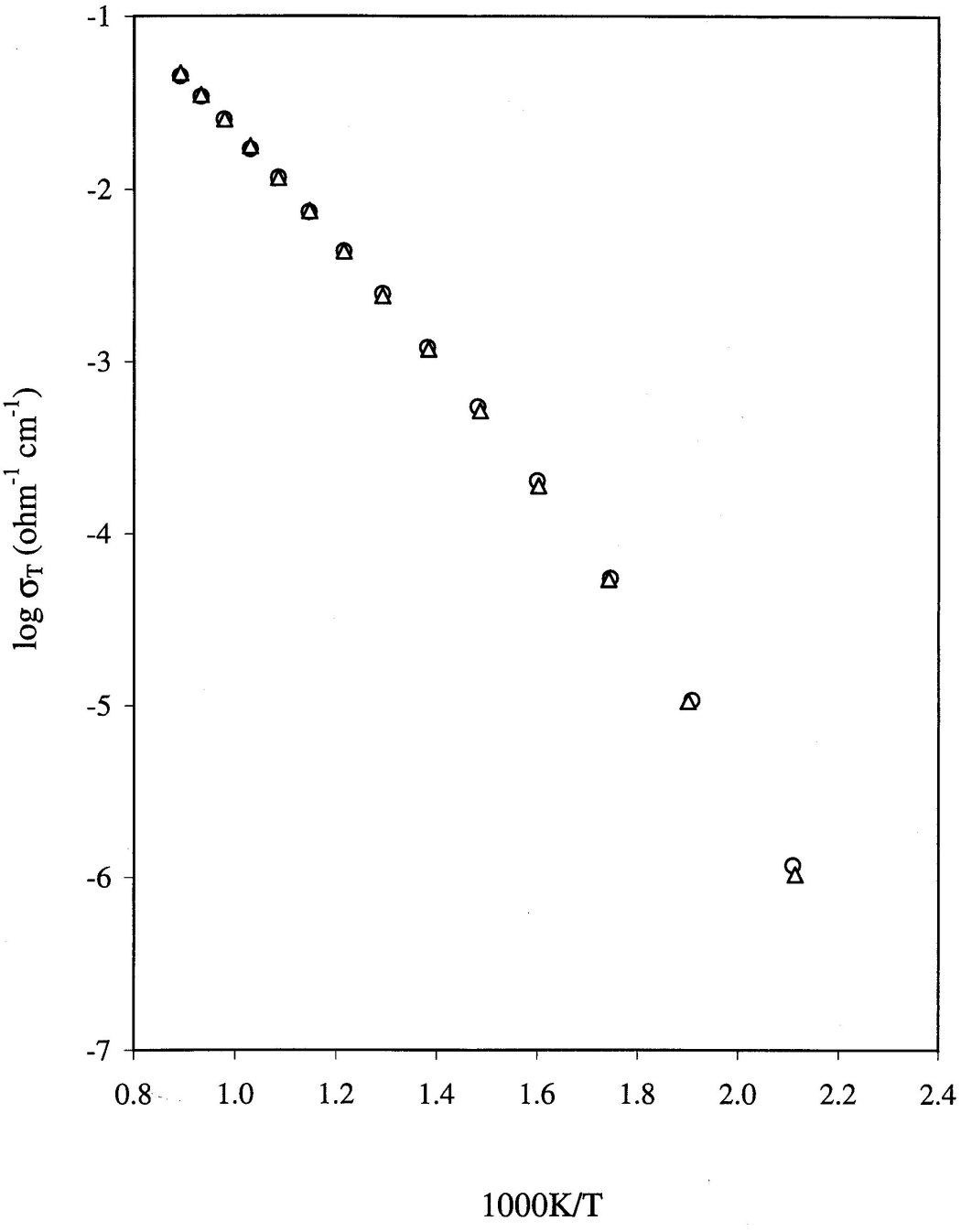

Figure 4 : Arrhenius plots of $Bi_{23}As_4O_{44.5}$ in air (○) and nitrogen (Δ).

These materials show reversible conductivity behavior in heating and cooling cycles. Curvature was observed in the Arrhenius plots. Figure 5 shows Arrhenius plots of xBi_2O_3-As_2O_5, $5 \leq x \leq 7$ during the first cooling cycle. The conductivity values range from 10^{-7} to 10^{-2} $ohm^{-1}cm^{-1}$ between 200 and 850°C with an activation energy of 0.75 eV. The Arrhenius plot of YSZ is included for comparison. Generally, at temperatures ≤ 300°C, the materials studied show decreasing conductivity in the order:

5.75:1 ≈ 5.667:1 > 6:1 ≈ 5.5:1 > 7:1 > 5:1

Above 600°C, the material of composition $7Bi_2O_3$-As_2O_5 has comparable conductivity to that of the others. The change in slope could be associated with the different mechanism taking place in conduction at higher temperature. Similar activation energies were obtained in compositions of 5:1, 5.667:1, 5.75:1 and 6:1 indicating that the charge carriers in these materials which have similar crystal structure could be identical.

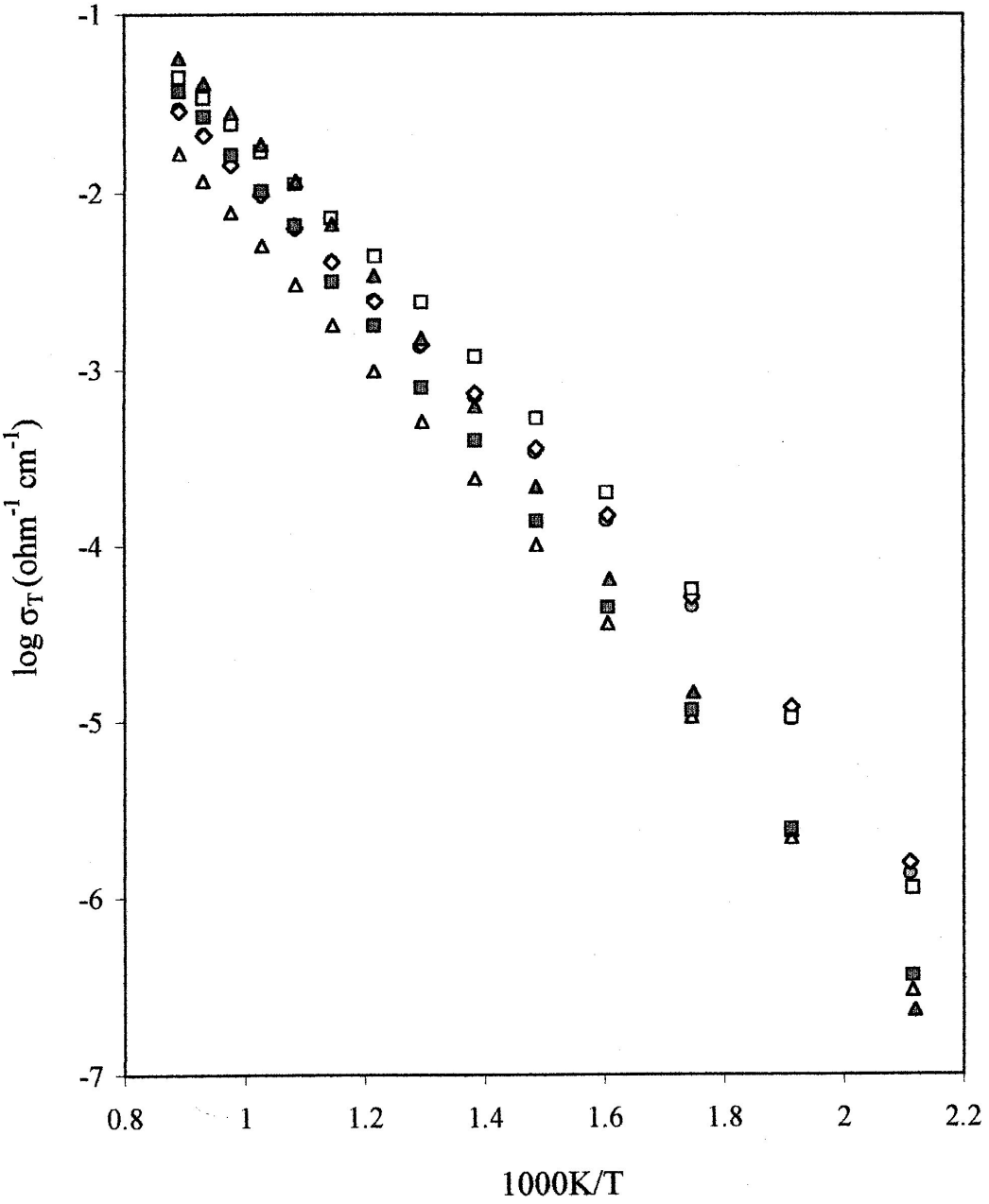

Figure 5 : Arrhenius plots of xBi_2O_3-As_2O_5 binary system, $5 \leq x \leq 7$.
Δ $x = 5$; • $x = 5.5$; ◊ $x = 5.667$; □ $x = 5.75$; o $x = 6$; ▲ $x = 7$; ■ YSZ

Among the materials studied in Bi_2O_3-As_2O_5 binary system, $Bi_{23}As_4O_{44.5}$ has the highest conductivity: 5.66 x 10^{-5} ohm^{-1} cm^{-1} at 300°C. The conductivity values obtained for the materials studied, except for Bi_5AsO_{10}, are comparable to that of YSZ, which is used as the electrolyte material in solid oxide fuel cell at present. The activation energies in the system where Bi/As = 5.5, 5.75 and 6 are also comparable to that of YSZ, 0.8 eV (Figure 5).

IR and SEM studies

The IR absorption spectra of xBi_2O_3-As_2O_5 binary system, $5 \leq x \leq 7$ are shown in Figure 6. The strong broad absorption at ~3440 cm^{-1} and a medium absorption band at ~1635 cm^{-1} correspond to the O-H stretching and bending mode, respectively. This is due to moisture picked up during the process of KBr disc preparation.

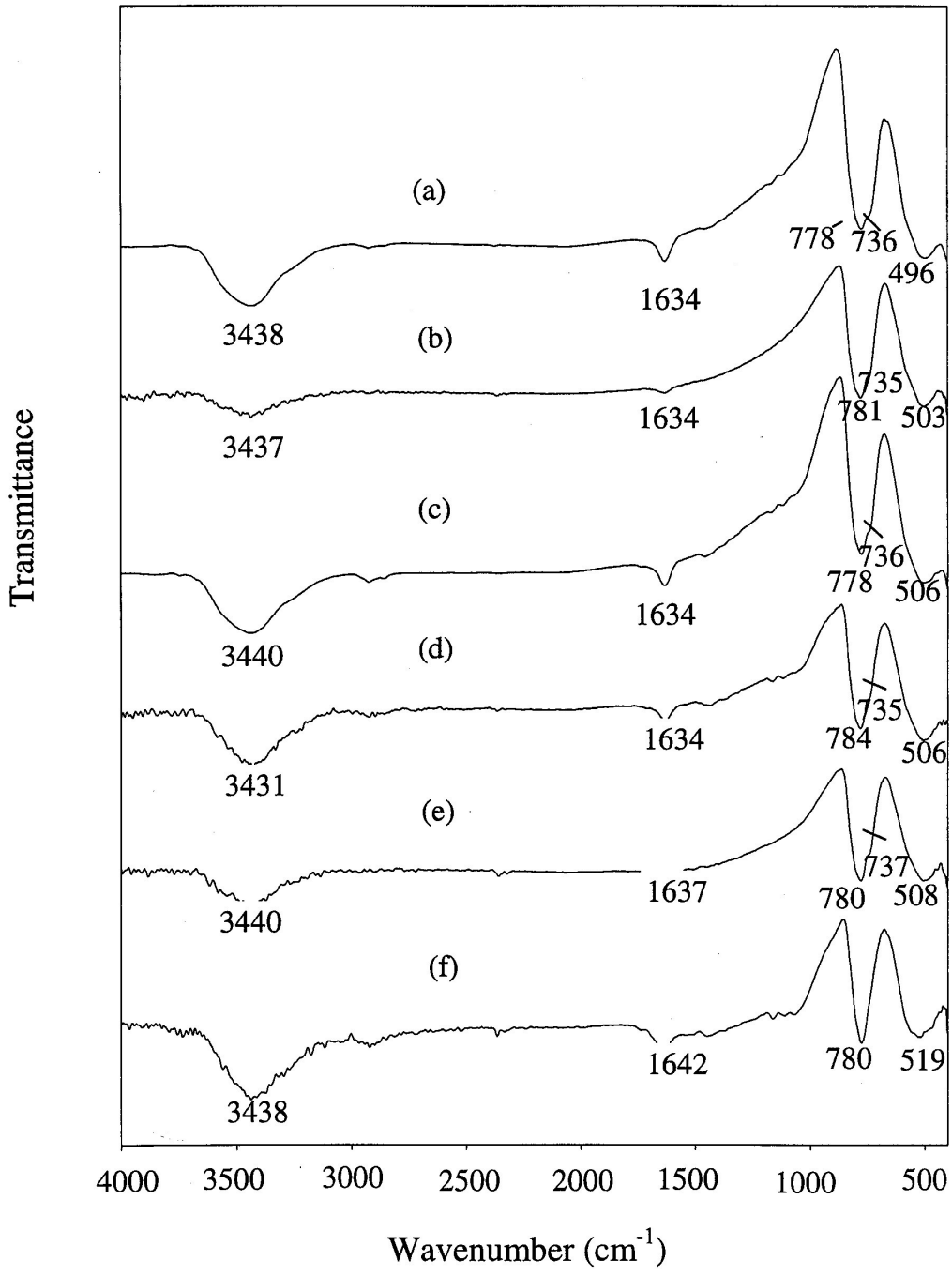

Figure 6 : IR spectra of xBi_2O_3-As_2O_5 binary system, $5 \leq x \leq 7$.
(a) $x = 5$, (b) $x = 5.5$, (c) $x = 5.667$, (d) $x = 5.75$, (e) $x = 6$, (f) $x = 7$

The IR spectra of xBi_2O_3-As_2O_5 binary system, $5 \leq x \leq 7$ show intense bands at ~780 cm^{-1} and ~500 cm^{-1}, which are assigned to ν(As-O) type of vibration [11]. The different Bi content in these materials did not result in noticeable variations in their IR spectra. At $5 \leq x \leq 6$, a weak shoulder at ~736 cm^{-1} was observed, which is absent when $x = 7$. This implies that the crystal structure of Bi_7AsO_{13} is different from the other materials studied in Bi_2O_3-As_2O_5 binary system.

From the results obtained in scanning electron microscopy (SEM) on single phase materials, it appears that there was no significant change in particle size and morphology with the increase of Bi content in these materials.

Conclusions

Solid solutions were obtained in xBi_2O_3-As_2O_5; $5 \leq x \leq 6.25$. These materials crystallize in triclinic symmetry. They appear to be thermally stable and behave as oxide ion conductors, with conductivity and activation energies comparable to that of YSZ.

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